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# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

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|--|--|------------------------|--|---|--|
| Given Name (first and middle [if any])   |  | Family Name or Surname |  | Residence<br>(City and either State or Foreign Country) |  |
| James M.   |  | Tour                   |  | Bellaire, TX  |  |
| Additional inventors are being named on the 1 separately numbered sheets attached hereto   |  |                        |  |   |  |
| TITLE OF THE INVENTION (500 characters max)  |  |                        |  |   |  |
| NOVEL FLAME RETARDANT VINYL POLYMERS   |  |                        |  |   |  |
| Direct all correspondence to: CORRESPONDENCE ADDRESS   |  |                        |  |   |  |
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| ENCLOSED APPLICATION PARTS (check all that apply)  |  |                        |  |   |  |
| <input checked="" type="checkbox"/> Specification Number of Pages  |  | 10                     |  | <input type="checkbox"/> CD(s), Number                  |  |
| <input type="checkbox"/> Drawing(s) Number of Sheets   |  |                        |  | <input checked="" type="checkbox"/> Other (specify)     |  |
| <input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76   |  | POSTCARD; CHECK        |  |   |  |
| METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT   |  |                        |  |   |  |
| <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.   |  |                        |  | FILING FEE AMOUNT (\$)                                  |  |
| <input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees.   |  |                        |  |   |  |
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| The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.          |  |                        |  |   |  |
| <input type="checkbox"/> No.   |  |                        |  |   |  |
| <input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: FAA / R13940-416000      |  |                        |  |   |  |

Respectfully submitted,

[Page 1 of 2]

SIGNATURE Hugh R. Kress

TYPED or PRINTED NAME Hugh R. Kress

TELEPHONE 713-650-2714

Date 06/20/03

REGISTRATION NO.

(If appropriate)

Docket Number:

36,574

11321/P067V1

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Docket Number 11321-P067V1

| INVENTOR(S)/APPLICANT(S)               |                   |   |
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[Page 2 of 2]

Number \_\_\_\_\_ of \_\_\_\_\_

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## Novel Flame Retardant Vinyl Polymers

### Description of the invention:

The invention is a new polymeric flame retardant, derived from a bisphenol C (BPC) analogue unit that has one or more vinyl pendants for effecting a vinyl polymerization where the vinyl might emanate from the aryl ring or come via an acroyl unit off one of the phenolic groups. We call this a BPC analogue; however, they may or may not bear the phenolic units. The 1,1-dichloro-2,2-diphenylethane unit (or its precursor, the 1,1,1-trichloro-2,2-diphenylethane) is the critical portion. Note that the chloro units could be substituted with other halogens and the phenyl units with other aromatics or substituted benzenes. This could be used as the exclusive monomer in the system or as a co-monomer along with other vinyl monomers. Conversely, the BPC-derived vinyl (including acroyl) polymer or co-polymer could be blended with other plastics to induce flame retardancy to the system. The commercial application of this flame retardant to materials of construction in common modes of transportation such as airplanes, helicopters, trains, buses, trucks, and automobiles will produce increased safety factors in crashes and wrecks, allowing passengers to escape before succumbing to the lethal effects of smoke and/or fire. It is also anticipated that this material could be used in blends used in the materials of construction of buildings and homes to impart some protection to residents and occupants in case of a fire, and in electronics equipment housings to prevent catastrophic fires from electrical shorts in equipment.

A novel flame retardant polyacrylate or other vinyl polymer has been synthesized with a pendant bisphenol C-analogue functionality that is itself highly non-flammable and can be used as the sole component for a plastic or may help to impart flame resistance when blended with a polymer that is normally highly flammable. The new flame retardant polymer can be used as is in the blend with no need for the addition of synergists that are normally used to help impart flame resistance to plastics. The invention is a new polymeric flame retardant polymer, derived from a bisphenol C (BPC) unit that has one or more vinyl pendants for effecting a vinyl polymerization. This could be used as the exclusive monomer in the system or as a co-monomer along with other vinyl monomers. Conversely, the BPC-derived vinyl polymer or co-polymer could be blended with other plastics to afford flame retardancy to the system. The main difference between this approach and other BPC systems is that the approach here uses the BPC as a pendant group in a vinyl polymerization, thereby permitting the formation of higher molecular weight systems that will lend themselves to both thermoplastics and thermosets (upon addition of a suitable crosslinker). This can be used in conjunction with nanoclays, Teflon, chlorinated polyethylene, or other additives, to impart anti-drip features. Also, there is the possibility that this pendant moiety can be directly attached to polystyrene and its derivatives using a 2,2,2-trihalo-1-aryl-1-ethanol intermediate in the presence of acid (Lewis or Brönsted) followed by a dehydrohalogenation. The dehydrohalogenation could be effected before polymer deployment or more simply in the fire scenario through in situ thermal elimination.

This research was funded by the FAA with the intention that new flame retardant additives would be used in aircraft materials of construction. The plastic blend containing the flame retardant polymer can potentially be molded into panels or structural components to be used in different aircraft applications. This new material has potential wide spread use in many various transportation materials of construction applications where plastics are already being used. The existing blends do not perform as well as the blends made with this new flame retardant polymer. It is expected that the use of the inventive flame retardant polymer will lower the cost of production of these materials of construction in the transportation industry and will lead to a reduction in the loss of life due to smoke inhalation and fire in accidents, wrecks, crashes, and other mishaps. Materials made with this new flame retardant polymer should have utility in materials of construction in airplanes, trains, buses, trucks, helicopters, and automobiles. It is also anticipated that this material could be used in construction of buildings and homes to impart some protection to residents and occupants in case of a fire, and in the housings of electronic equipment which must be flame retardant to prevent catastrophic fires due to a small short circuit.

The advantage of the invention is that existing plastics and vinyl polymers in particular can be easy to process and widespread utility, but they have are also very flammable; thus they need to be treated with heavy doses of flame retardant additives. Interestingly, in our recent UL 94 test applications, these vinyl-derived polymers do not burn. It is not even a matter of their self-extinguishing, but even upon continued application of the flame, the polymers do not burn. And achieving high molecular weights coupled with easy processing makes them quite attractive as candidates for flame retardant applications.

The new material is made through the attachment of a vinyl group to the aryl moiety of the system. This can be done through an acryl group being added to the monomer, or simple a vinyl pendant on the aryl ring of the 1,1-dichloro-2,2-diphenylethene. This can be accomplished in 3-4 synthetic steps for monomer preparation, followed by polymerization. Or one could functionalize polystyrene directly as described above.

The advantage of the inventive polymeric material is that its physical properties can be fine tuned by using different monomers in its preparation, or by using additives to achieve the exact characteristics that are desired. There may be the need for an anti-drip additive in the thermoplastics such as nanoclays, Teflon, or chlorinated polyethylene. Without these additives, dripping occurred upon second heat source application, as is expected from a thermoplastic; encouragingly, the dripping polymer does not ignite cotton, thereby leading to a successful fulfillment of the UL 94 industry standard test.

The BPC analogues can be copolymerized with other monomers to help impart greater impact resistance or other desirable features. The polymerization can be effected by several methods as described above.

**Grant or Contract Number:**

R13940- 416000; contract # 02-G-023 with the Federal Aviation Administration



## Technical Section

### Development of Asymmetrical Flame Retardant Bisphenol C Polymers (ABPC) Introduction

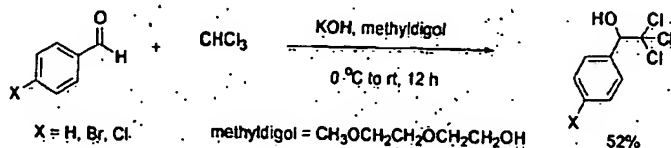
The development of processible flame retardant polymers has been a major challenge for both industrial and academic chemists. Most flame retardant polymers are highly rigid structures containing large amounts of aromatic char forming functionality. These polymers tend to be hard to process and have high melting temperatures, which result in elevated cost and rigorous processing methods. The incorporation of flexible linkers for making processible polymers, which are found in vinyl addition polymers, are not usually considered flame resistant, and therefore is not usually a suitable options for flame retardant polymers. Due to the excellent flame retardant characteristics of bisphenol C (BPC), we have made new asymmetric BPC (ABPC) monomers with an easily polymerized acrylate functional group. (In this context, we do not use the term asymmetric to mean chiral, but rather that the molecule is functionalized asymmetrically—the two ends have differing functionalities).

Acrylic polymers are known for their resistance to heat, sunlight, and weathering which makes them an excellent candidates for flame retardant polymers.<sup>1</sup> The approach to making these acrylate polymers was to incorporate the flame retardant BPC as a pendant group hanging off the acrylate skeleton. This has produced a flame retardant and processible polymer that can be melted and molded into a new flame resistant material.

### Results and Discussion

The new asymmetric bisphenol C (ABPC) structures are made from cheap and readily available starting materials. The first step is to produce the trichloroethanol product often referred to as the carbinol. The carbinol is synthesized by slowly adding a solution of potassium hydroxide and methyldigol (diethylene glycol monomethylether) to a stirring solution of benzaldehyde and chloroform chilled at 0 °C (Reaction 1).

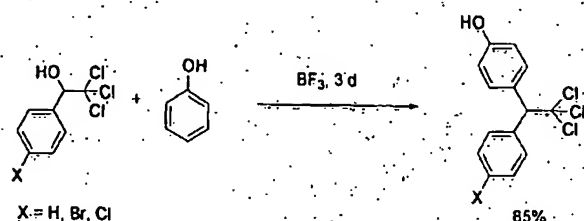
#### Reaction 1





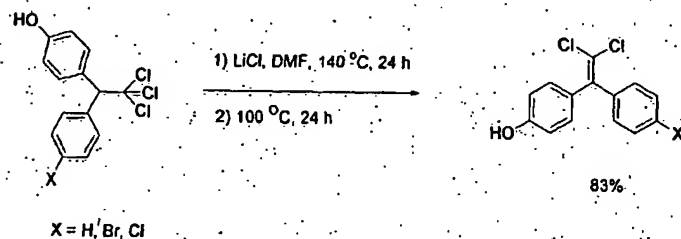
The resulting carbinol is purified by vacuum distillation and reacted with phenol in the presence of  $\text{BF}_3$  gas over several days to yield the asymmetrical DDT molecule. This process takes several daily additions of  $\text{BF}_3$  and mechanical stirring to afford the dark viscous mixture, which is then purified by column chromatography.

#### Reaction 2



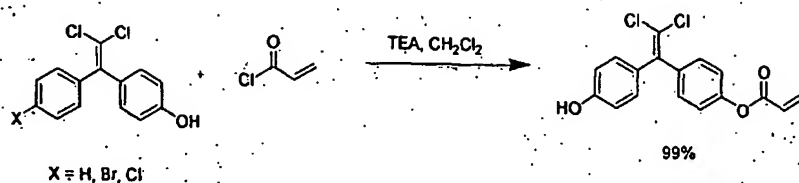
The dehydrohalogenation of the ABPC is done using the standard procedure of lithium chloride addition in DMF at  $140^\circ\text{C}$  for 24 h then slowly decreasing the heat to  $100^\circ\text{C}$  (Reaction 3).

#### Reaction 3



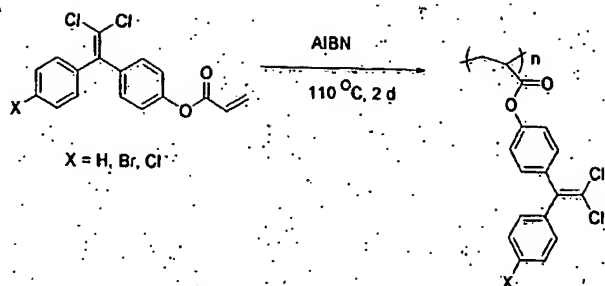
The final step to afford the acrylate monomer is the addition of acryloyl chloride to a solution of the ABPC, triethylamine and in methylene chloride (Reaction 4).

#### Reaction 4



The acrylate polymer is made by a bulk polymerization with 2,2'-azobisisobutyronitrile (AIBN) at  $110^\circ\text{C}$  for 2 d (Polymerization 1)

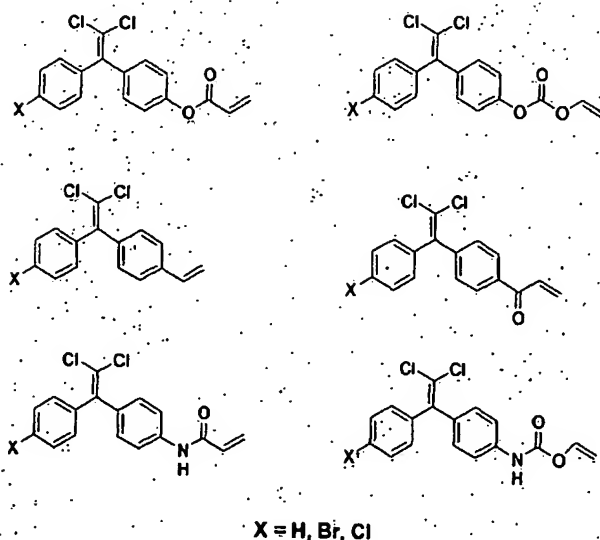
### Polymerization 1



Preliminary burn methods conclude this polymer works well as a flame resistant material. The polymer dripped, but did not ignite the cotton when it subjected to the HVUL-94 flame test. With the addition of the anti-drip additive, 1 wt% PTFE, the sample did not drip at all. The polymer is considered to be a V-0 material according to the UL-94 test for flammability of plastic materials.

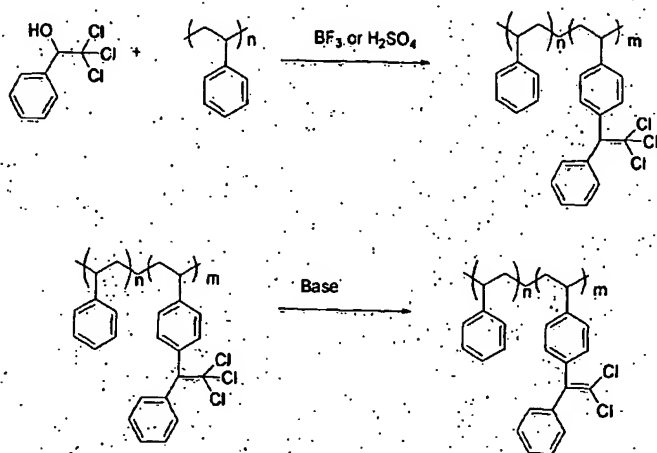
In addition to the above mentioned vinyl polymers that have been already made, the following is a list of potential vinyl addition polymers that could be made using this ABPC core (Figure 1).

Figure 1



Another potential use for the carbinol is to impart flame retardancy to flammable polymers such as polystyrene. By taking the carbinol and reacting with polystyrene in the presence of  $\text{BF}_3$  or sulfuric acid, followed by a dehydrohalogenation reaction with base should give the more stable flame retardant polymer (Reaction 5 & 6).

### Reaction 5 & 6

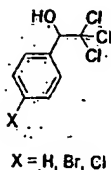


### Burn Results

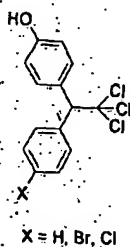
| Additive                  | First Ignition <sup>a</sup><br>(sec) | Observed Dripping <sup>b</sup> | Second Ignition <sup>a</sup><br>(sec) | Observed Dripping <sup>b</sup> | UL-94 Rating |
|---------------------------|--------------------------------------|--------------------------------|---------------------------------------|--------------------------------|--------------|
| Polyacrylate A            | 0, 0                                 | No, No                         | 1, 1                                  | No, Yes                        | V-0, V-0     |
| Polyacrylate A, 1wt% PTFE | 0, 0                                 | No, No                         | 0, 0                                  | No, No                         | V-0, V-0     |

<sup>a</sup> Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. <sup>b</sup> Indicates that molten polymer did (Y) or did not (N) drip on to cotton patch underneath ignited bar during UL-94 test. <sup>c</sup> Indicates ignition of cotton patch underneath ignited bar of plastic. <sup>d</sup> Indicates time that only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition. \* Wt % based on halogen content

## Experimental

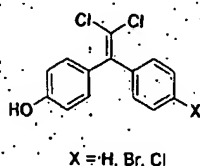


**2,2,2-Trichloro-1-phenyl-ethanol (X, JLJ-IV-55, 65, 67, 71, 73, 79, 91, 103, 133).<sup>2</sup>** To a 250 mL three necked round bottom flask, equipped with a stir bar and addition funnel and purged with nitrogen was added benzaldehyde and chloroform. Potassium hydroxide (1.2 equivalents) (KOH) dissolved in diethylene glycol monomethyl ether (methyl digol) was added dropwise via the addition funnel. The reaction mixture was cooled to 0 °C while the KOH and methyl digol was added slowly over 6 h. The reaction was then allowed to warm to room temperature with stirring for 12 h. The reaction was then poured into cold water and diluted with methylene chloride. The two layers were separated and the organic layer was washed with HCl (0.1 N), and H<sub>2</sub>O (2 x). The organic layer was dried over magnesium and filtered through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via vacuum distillation 85 – 110 °C (1 atm).

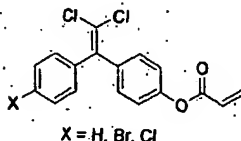


**2-(*p*-Hydroxyphenyl)-2'-(phenyl)-1,1,1-trichloroethane (X, JLJ-IV-85, 87, 93, 97, 107, 113, 125, 135, 145).<sup>2</sup>** To a 100 mL three necked round bottom flask, equipped with a stir bar, mechanical stirrer, and a gas inlet tube was added X and phenol (0.98 equivalents), the flask was sealed with a septa and boron trifluoride (BF<sub>3</sub>) was bubbled into the solution for 20 m, with constant stirring. The thick solution was stirred vigorously and BF<sub>3</sub> was bubbled into the reaction mixture every 12 h for 3 to 5 days. The reaction was then poured into cold water and diluted with ethyl acetate. The two layers were separated and the organic layer was washed with K<sub>2</sub>CO<sub>3</sub> (1 M, 2 x) and H<sub>2</sub>O (2 x). The organic layer was dried over magnesium and filtered

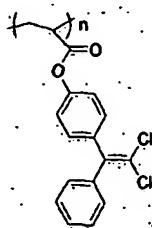
through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via column chromatography (9:1; Hexane/Ethyl acetate).



**2-(p-Hydroxyphenyl)-2'-(phenyl)-1,1-dichloroethane (X, JLJ-IV-88, 89, 94, 121, 126, 127, 136).<sup>3</sup>** To a 250 mL round bottom flask, equipped with a stir bar and reflux condensor and purged with nitrogen, was added 2-(p-hydroxyphenyl)-2'-(phenyl)-1,1,1-Trichloroethane, KOH (7 equivalents), and MeOH (150 mL). The flask was then sealed under nitrogen with a septum and heated to reflux for 24 h. The reaction mixture was then diluted with ethyl acetate. The organic layer was washed with H<sub>2</sub>O (3×) and the aqueous layer was then extracted with ethyl acetate (3×). The organic layers were combined and dried over magnesium sulfate and filtered through filter paper. Solvent was then removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h.



**Acrylic acid [2-(p-hydroxyphenyl)-2'-(phenyl)-1,1-Dichloroethane] ester (X, JLJ-IV-90, 101, 105, 111, 128, 131, 137).** To a 100 mL round bottom flask equipped with a stir bar and purged with nitrogen was added the acrylate monomer X. The reaction flask was evacuated and backfilled with nitrogen (3×). Methylene chloride and triethylamine (1.5 equivalents) were added to the flask via syringe and cooled on an ice bath. Acryloyl chloride (1.1 equivalents) was slowly added dropwise via syringe. The ice bath was removed and the resulting solution was allowed to warm to room temperature and stirred for 12 h. The reaction was then quenched by opening the flask to air, and the reaction mixture was rotovaped to dryness. The final product was isolated via column chromatography (9:1; Hexane/Ethyl acetate).



**Polyacrylate A (A, JLJ-IV-102, 123, 129, 139, 141, 147, 151).** To a 100 mL round bottom flask equipped with a stir bar was added the acrylate monomer and 2,2'-azobisisobutyronitrile (AIBN: 1000/1; monomer/initiator) and sealed with a septa under nitrogen. The reaction flask was evacuated and backfilled with nitrogen (3×). The reaction mixture was then placed in an oil bath at 110 °C and stirred for 2 d. The reaction was then cooled to room temperature, dissolved in chloroform and precipitated in methanol. (X= H)  $M_w$ : 607, 300;  $M_n$ : 321,200. (X=Cl)  $M_w$ : 280, 600;  $M_n$ : 110, 000.

### References

- (1) Horn, M. B. *Acrylic Resins*; 2 nd ed.; Reinhold Publishing Corporation: New York, 1962.
- (2) Wootton, R.; Goodford, P. J.; Hudson, A. T.; Sheppey, G. C. *J. Med. Chem.* **1976**, *19*, 1239-1247.
- (3) Hubacher, M. H. *J. Org. Chem* **1959**, *24*, 1949-1951.

What is claimed is:

1. A flame retardant polymeric material comprising bisphenol C analogue monomers, wherein the bisphenol C analogue monomers comprise at least one vinyl pendant.
2. The material of Claim 1, wherein the vinyl pendant is operable for effecting a vinyl polymerization.
3. The material of Claim 1, wherein the bisphenol C analogue monomers are co-polymerized with a different monomer to form a flame retardant co-polymer.
4. The material of Claim 1, wherein the bisphenol C analogue is the exclusive monomer in a flame retardant polymer.
5. The material of Claim 3 or 4, wherein the flame retardant polymer is blended with another polymer.
6. The material of Claim 1, further comprising an anti-drip additive.

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